Thermal oxidative stability of polyanilines

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A B S T R A C T

This paper deals with thermal ageing of polyaniline obtained from plasma or chemical ways. FTIR analyses suggest the formation of stable carbonyl compounds in both cases. The plasma polyaniline degrades clearly faster than its chemical analog which is discussed from structural considerations. The consequences of thermal ageing on the surface properties monitored by Water Contact Angles (WCA) are also considered and explained as the overlap of an "oxidation" component that decreases WCA and a "crosslinking" component (only observed in plasma polyaniline) responsible for the WCA increase.

1. Introduction

Conjugated polymers (polyacetylene, polythiophene or polyaniline) display electrical and optical properties making them particularly interesting, for example, to design reliable sensor used to detect gaseous compounds [1].

The conventional (chemical or electrochemical) methods for synthesizing polyaniline involve however various kinds of hazardous chemicals. Plasma synthesis has emerged as a promising alternative where the monomer is activated in gaseous phase. This solvent-free process is hence considered as more environmental friendly.

In the case of chemical (conventional) polyaniline, the durability in electrical field [2], water [3], strong oxidizing medium [4], or thermo-oxidative conditions [5] was already studied but the issue to exploit those data to predict lifetime of plasma polyaniline remains for us open. Plasma synthesis actually induces some side effects since the structure of plasma polyaniline appears quite different from polyaniline synthesized by conventional chemical and electrochemical routes [6,7] and the issue of its long-term stability remains open [8].

It is considered that plasma polymers, that are crosslinked during or after their synthesis, would be more stable than their organic analogs prepared by conventional methods [9]. This assumption is questionable for at least two reasons:

- there is no direct correlation between crosslinking and higher chemical stability. One can for example quote the comparison between two unsaturated substrates with comparable levels of double bonds: polybutadiene (a rubbery polymer) oxidizes slower than polydicyclopentadiene which is a glassy network [10].
- the plasma synthesis actually induces the transformation of monomer in gas phase in unstable species (ions, radicals) so that the structure of plasma polymer is not strictly the same than the structure of the corresponding polymer obtained by a conventional way.

We are thus interested in investigating in which extent the chemical structure depending on the synthesis method influences the stability of a plasma polymer in comparison with a conventional one. For that purpose, the thermal ageing of two kinds of polyanilines (synthesized either from plasma or conventional method) is compared in a multiscale study dealing with both chemical (studied by FTIR and XPS) and macromolecular (studied by water contact angle measurements) properties, those techniques being adapted for both polyaniline: the chemical one (a linear polymer) and the plasma one (a crosslinked network synthesized as a coating *i.e.* in small quantity).

2. Experimental

2.1. Commercial chemical polyaniline deposition

Polyaniline (emeraldine base - CAS Number 25233-30-1 - average Mw ~ 100,000) was supplied from Sigma Aldrich (ref 576379). Emeraldine base (EB) was dissolved in THF and was casted on the substrates (KBr plates or glass) prior to ageing.

It was verified by FTIR analyses that the chemical structure of commercial EB was the same than that of synthesized EB.

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2.2. Plasma polyaniline synthesis and deposition

Pulsed plasma technique was employed for the synthesis and deposition of plasma polymerized aniline (pp-ANI) thin films. The reactor consists of a cylindrical aluminium capacitively coupled chamber with two parallel circular electrodes (MG300S, Plassys). The latter are 30 cm in diameter and 1 cm thick, separated by 12.8 cm. The substrates were placed on the lower powered electrode. The substrates were Si/SiO_2 wafer, glass or KBr pellet according to the analysis technique used afterwards. A primary pump and a turbomolecular pump allowed achieving a 5×10^{-6} Torr ultimate pressure in the chamber. The monomer vapour was then introduced into the reactor from a glass tube containing aniline liquid (Aldrich, CAS Number 62-53-3) and maintained at room temperature (20 °C). During the polymerization process, the monomer vapour pressure into the reactor was fixed at 0.02 Torr using a throttle valve and was measured using a Pirani gauge. The pulsed plasma discharge was sustained by a radio-frequency (13.56 MHz) generator using a manual matching network. The polymer has been synthesized using a discharge time (t_{on}) of 17 µs and a post-discharge time (t_{off}) of 150 µs leading to a pulse frequency (f) of 6 kHz and a duty cycle (dc) (corresponding to the ratio of discharge time to period) of 10%. Two discharge powers have been used: 10 and 50 W.

Between each deposition, the reactor was cleaned during 10 min using oxygen and then argon plasmas (RF power = 100 W, pressure = 0.01 Torr, flows of O_2 or Ar = 20 standard cubic centimeters per minute).

The initial chemical structure of pp-ANI has been characterized in a previous work using Fourier Transform Infra-Red, X-ray Photoelectron and UltraViolet-Visible spectroscopies [7].

2.3. Ageing conditions

Samples were aged:

- at room temperature (for plasma polyaniline),
- in ventilated ovens (AP60 supplied by SCS) at temperatures ranging from 120 to 200 °C (for chemical polyaniline).

2.4. Characterization techniques

2.4.1. FTIR analyses

FTIR measurements were performed using a Frontier 100 apparatus (PerkinElmer) by averaging 32 scans over the range of 400–4000 cm^{-1} at a resolution of 2 cm^{-1}. pp-ANI and EB were analyzed in transmission mode using KBr pellets (99.99%, Sigma-Aldrich) and KBr plates as substrates respectively.

2.4.2. Water contact angle measurements

In this work, the water contact angle (WCA) measurements were realized thanks to a Ramé-Hart goniometer at room humidity and temperature, using a water volume of 3 µL. The WCA values are the average of six measurements taken at different locations on the layer surface. For these measurements, pp-ANI and EB were deposited onto glass substrates.

2.4.3. XPS measurements

The chemical nature of the plasma polymers, in particular their oxygen content, deposited onto Si/SiO_2 wafers (Siltronix, France) was also determined by XPS (Kratos Axis Nova, UK) at the Institut des Matériaux de Nantes, France. The photoemission was excited by a monochromatic Al Kα beam. Survey scans (1200 - 0 eV) were recorded with steps of 0.5 eV with an analyzer pass energy of 160 eV. The analysis depth and area of pp-ANI were around 10 nm and 400 µm × 800 µm respectively. The elements quantification accuracy was 5%.

3. Results

3.1. Ageing of the chemical structure

We have first studied the ageing of pp-ANI under ambient atmosphere using FTIR spectroscopy. Fig. 1 depicts the spectra of pp-ANI synthesized at 10 W (Fig. 1a) or 50 W (Fig. 1b). The FTIR bands assignment of unaged pp-ANI (called "initial") is given in Table 1 and compared with chemical polyaniline (emeraldine base) [4].

The FTIR spectrum of pp-ANI presents most of the characteristic bands of emeraldine base with, however, some additional bands. The band at 2930 cm^{-1}, corresponding to saturated C–H stretching vibrations, shows the partial loss of aromaticity during plasma polymerization. It proves the fragmentation of the monomer in the plasma phase through π-bond scission or ring opening. Moreover, the bands at 750 cm^{-1} attributed to ortho di-substituted aromatic ring and at 695 cm^{-1} assigned to meta di-substituted aromatic ring give evidence of crosslinking of pp-ANI, contrary of the linear structure of emeraldine base [3,6,11,12]. In conclusion, pp-ANI is formed by the association of several monomer fragments leading to a more or less disordered and crosslinked structure.

pp-ANI ageing leads to several changes of the FTIR spectra. A new band appears at 3100-3600 cm^{-1} associated to hydroxyl groups. The appearance of a shoulder at 1600-1800 cm^{-1} shows the presence of carbonyl groups in aged pp-ANI. The formation of stable oxygenated products is evidenced by XPS analyses showing the increase of oxygen content in pp-ANI from 2.5% to 8.3% after 11 weeks of ageing when pp-ANI is elaborated at 10 W, and from 8.5% to 10.04% at 50 W. The intensity of these two bands increases with time. Moreover, a small increase of the band at 1600 cm^{-1} compared to that at 1500 cm^{-1} is observed, showing a loss of aromaticity with polymer ageing.

The rate of ageing depends on the chemical structure of the plasma polymer, namely the plasma parameters used to elaborate the polymer. Fig. 2 presents the evolution of the carbonyl and hydroxyl IR bands with time at the two studied discharge power (10 and 50 W).

Fig. 2 shows that layers elaborated at 10 W, the evolution with time of the two bonds (carbonyl and hydroxyl) is faster compared to 50 W. As shown in a previous work [4], more radicals are formed at high power due to a more important fragmentation leading to a higher crosslinked structure. Therefore, oxygen atoms can hardly diffuse through the layer, which decreases the ageing rate.

In order to compare with conventional polymer, we have also studied the ageing of commercial chemical polyaniline in its emeraldine base (EB) form. At first, EB appeared to be stable at room temperature. To assess the difference in stability, EB was aged at several temperatures higher than ambient one. Fig. 3 presents the FTIR spectra of emeraldine base after its ageing at 160 °C during 10 h, 30 h, 50 h and 100 h. The assignment of the bands is given in Table 1.

The most important changes are between 1000 and 2000 cm^{-1} (Fig. 3b). As for pp-ANI ageing, a shoulder appears in the region comprised between 1600 and 1800 cm^{-1} that is associated to carbonyl (C═O) stretching vibration. The intensity of this vibration increases with time. We can also note the increase of the bands at 1390 and 1430 cm^{-1} and the decrease of those at 1310 cm^{-1} and 1160 cm^{-1} with time.

The ageing of emeraldine base has also been studied at other temperatures. Fig. 4 presents the evolution of the carbonyl IR bands with time at three studied temperatures (120 °C, 160 °C and 200 °C). For simplicity, we will assume in the following that the growth of carbonyl band actually represents the overall oxidation process (i.e. that there is no loss of volatile oxidation products that should be quantified in addition).

The "degradation rate" r_{CO}, which is defined as the maximal slope from Fig. 4, is observed to increase with temperature. To illustrate the differences in ageing kinetics between pp-ANI and emeraldine base, the degradation rates are plotted in an Arrhenius diagram presented in Fig. 5

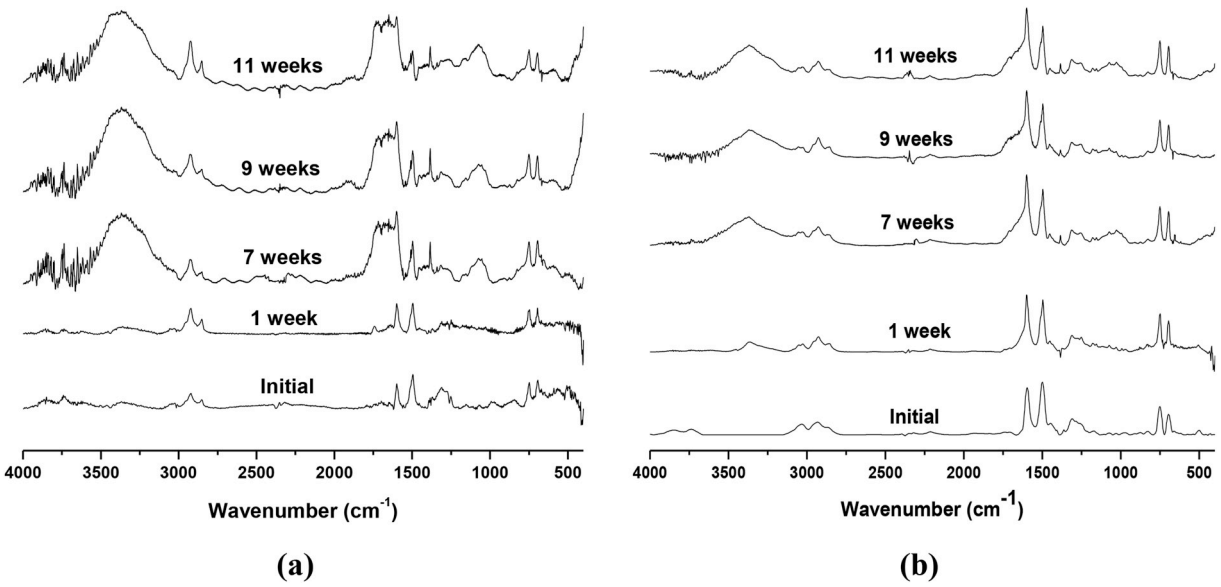


Fig. 1. FTIR spectra of pp-ANI during its ageing under ambient conditions and elaborated at (a) 10 W or (b) 50 W.

Table 1
Assignment of the IR bands for pp-ANI and emeraldine base.

Wavenumber (cm^{-1})	pp-ANI	Emeraldine base
695	1,3 di-substituted aromatic ring (meta)	
750	1,2 di-substituted aromatic ring (ortho)	
830		1,4 di-substituted aromatic ring (para)
1160		In-plane and out of plane aromatic C–H bending vibrations
1310	C–N stretching vibrations of secondary aromatic amine	C–N stretching vibrations of secondary aromatic amine
1500	Aromatic C⎯C stretching vibrations	C=C stretching vibrations of benzenoid ring
1600	Aromatic and aliphatic C⎯C stretching vibrations	C=C stretching vibrations of quinoid ring
2930	Saturated C–H stretching vibrations	
3030	Unsaturated C–H stretching vibrations	Unsaturated C–H stretching vibrations
3350	N–H stretching of secondary amine	
3100–3450		N–H stretching vibrations of secondary amine

(*N.B.*: the precise assessment of r_{CO} would require the knowledge of molar absorptivity of oxidation products, which is hard to determine given the relative complexity of mechanisms in the case of both polyanilines). It must be recalled that, for a given polymer, the temperature induces an increase of the global oxidation rate, but the effect is not necessarily the same for each elementary reaction (initiation, propagation, termination). Despite the subsequent limits in using Arrhenius equation to extrapolate degradation kinetics [13,14], we used it in a first approach to compare the possible oxidation kinetics of PANI EB at room temperature with the degradation kinetics of pp-ANI. An order of magnitude would be about 2.10^{-7} day^{-1} i.e. clearly lower than for pp-ANI (Fig. 2). The possible mechanistic reasons will be discussed later.

3.2. Ageing of surface properties

Fig. 6 shows the evolution of the water contact angle of pp-ANI layers synthesized at a discharge power of 10 W (Fig. 6a) or 50 W (Fig. 6b) and aged in air or under vacuum.

First, the initial value of WCA for pp-ANI is lower than that of PANI with a difference of about 5–8° according to the elaboration conditions. It may be explained by the presence of oxygenated species on the surface of the plasma polymer as evidenced by XPS analyses (see §3.1) contrary to the conventional polymer.

The WCA increases with time regardless of the power and the conditions of ageing. Then, the WCA of layers aged in air seems to exhibit a maximum and to decrease (mainly at 10 W) within the experimental uncertainties, whereas a plateau is obtained for films aged under vacuum. As it will be seen in the discussion section, the WCA decrease for pp-ANI elaborated at 10 W would be related to oxidation effects witnessed in Fig. 2.

4. Discussion

The aims of this section are to explain:

- the nature of chemical changes occurring in both polyanilines during their thermal ageing,
- the differences in degradation kinetics related to the elaboration process (chemical or plasma),
- the structure-properties relationships involved in the changes of WCA.

4.1. On the degradation mechanism

Let us start by recalling that oxidation is an in-chain radical mechanism involving the homolysis of covalent bonds, and the abstraction of hydrogen atoms participating to “weak” bonds. In polyaniline, the orders of magnitude of those bonds dissociation energies are around 360 kJ mol^{-1} for N–H bonds [15] and more than 400 kJ mol^{-1} for C–H bonds in aromatic rings [16].

This means that oxidation preferentially involves the N–H bonds first. A possible mechanism is presented in Scheme 1 in order to explain the formation of various kinds of carbonyl and hydroxyl products observed in Fig. 3: primary radicals would be hold by nitrogen atom. The resulting radicals can isomerize and react with oxygen to give, in several steps, a hydroperoxide [17]. The decomposition of this latter generates an alkoxy expected to decompose either into an alcohol or a ketone [18].

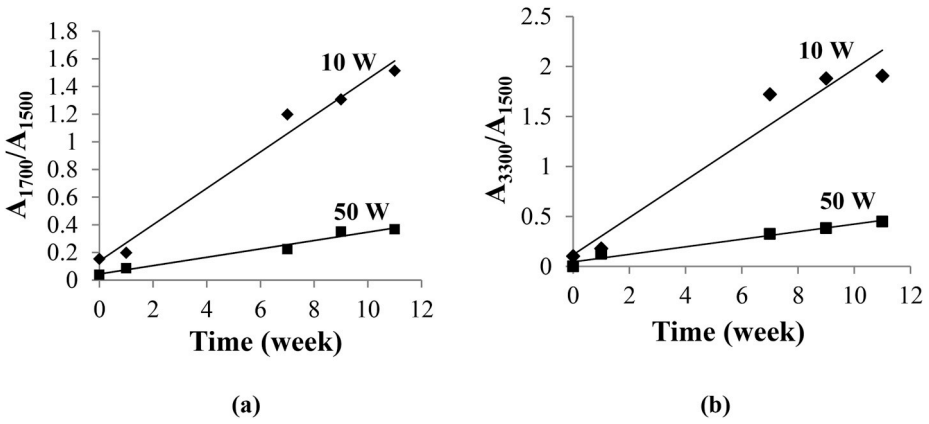


Fig. 2. Evolution of (a) carbonyl groups and (b) hydroxyl ones after ageing of pp-ANI elaborated at 10 W or 50 W.

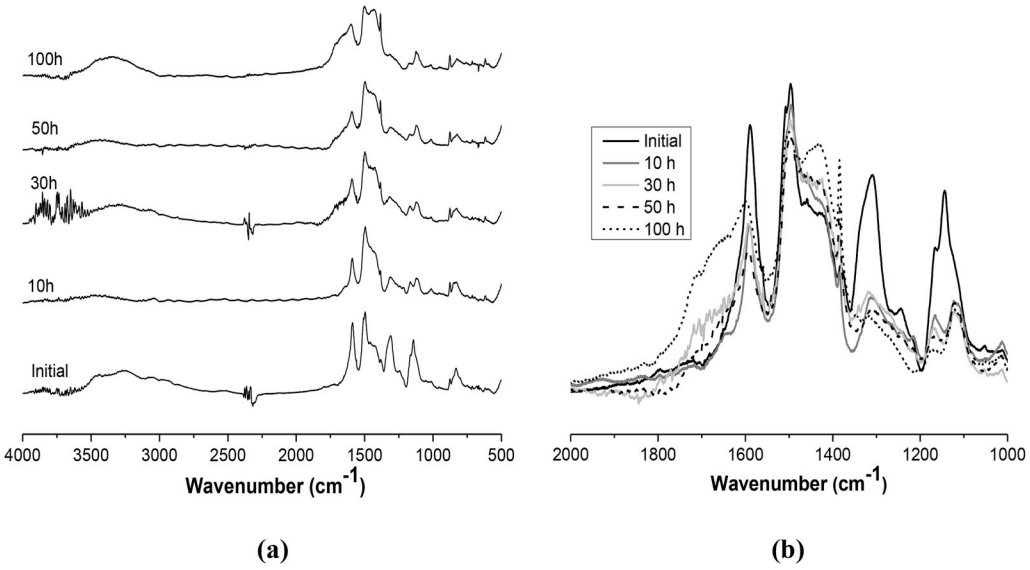


Fig. 3. (a) FTIR spectra of emeraldine base during its ageing at 160 °C, (b) zoom in on the region comprised between 1000 and 2000 cm^{-1}.

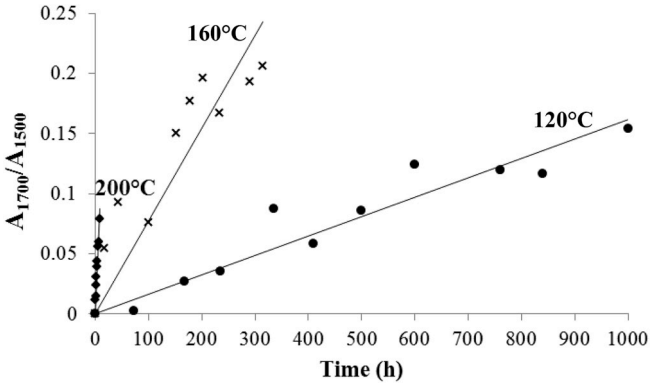


Fig. 4. Evolution of carbonyl groups of emeraldine base after its thermal ageing at 200, 160 and 120 °C.

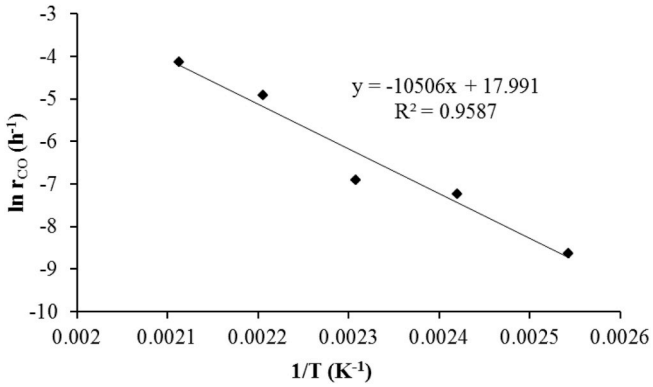


Fig. 5. Arrhenius diagram of the apparent degradation rate for emeraldine base.

Despite this is not presented here, it seems also possible that two peroxy radicals react together and give a carbonyl and an alcohol by a dismutation process [19].

It must be noted that the presence of aminyl radicals can possibly lead to nitroxides (>NO°) [20]. The latter are known to be very efficient stabilizers in several kinds of polymers and in particular polyolefins [21–23]. This latter fact can explain in part the relatively high stability of chemical polyaniline compared to pp-ANI (as it will be developed in the next paragraph). However, the possible stabilization by nitroxide seems to be limited since carbonyl and hydroxyl species are generated during the thermal ageing of emeraldine base.

The chemical structure of pp-ANI is usually considered to be in part

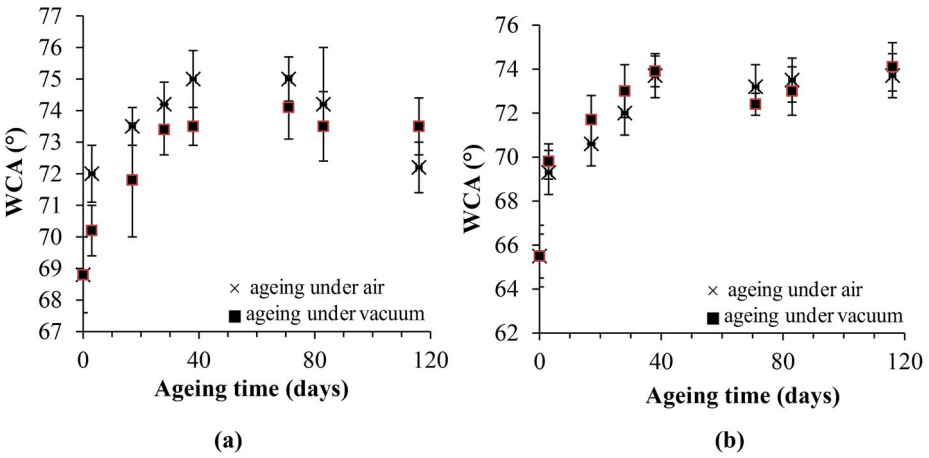
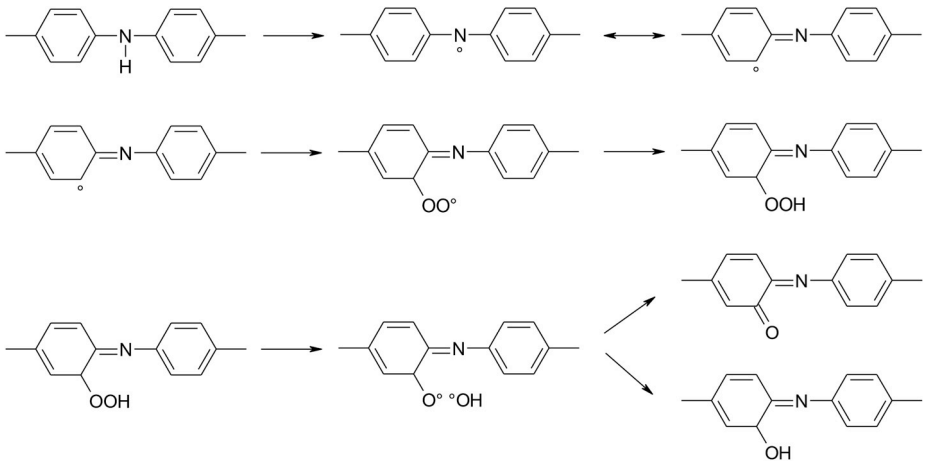


Fig. 6. Evolution of the WCA with time of pp-ANI layers elaborated at a discharge power of (a) 10 W or (b) 50 W.



Scheme 1. A possible mechanism for emeraldine base oxidation.

different than chemical polyaniline. Several kinds of structural irregularities are reported such as:

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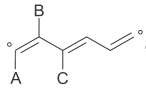
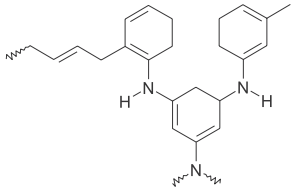
after π-bond scission, where R, R′ are either H atoms or secondary/tertiary carbon atoms,
- 

after aromatic ring opening, where A, B, C are the three possible positions of the amino group.

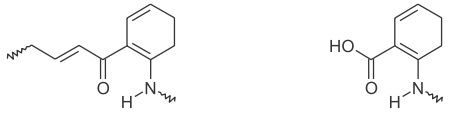
The final structure is quite complex but it seems that:

- part of aniline groups is preserved and degraded as presented in Scheme 1,
- some structural defects co-exist such as:

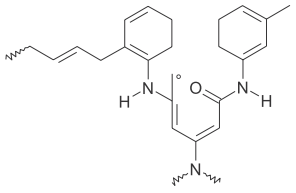


In terms of chemical reactivities, it is clear that:

- allylic C–H are particularly oxidizable (in particular because of a weak bond dissociation energy value [24]) and give unsaturated carbonyl species (α-β unsaturated acids or α-β unsaturated ketones) [25]:



- C–H in α position of nitrogen atoms are also very oxidizable and give fairly unstable hydroperoxides generating later amides products [26]:



In other words, the broad absorption peak observed in degraded pp-ANI (Fig. 1) is the sum of several species being:

- either identical to those produced during the thermal degradation of emeraldine base (i.e. presented in Scheme 1),
- or species coming from the oxidation of defects (allylic C–H and C–H at the vicinity of nitrogen atoms). Those latter are quite unstable from a kinetic point of view as discussed later and contribute then to explain why pp-ANI undergoes a faster oxidation than its chemical analog.

Moreover, the degradation of pp-ANI is accelerated by the fact that a certain quantity of radicals exists in the "initial" structure resulting from the polymerization process. Therefore, the oxidation of pp-ANI can be considered as self-activated compared to that of conventional polyaniline where possible minor structural defects play the role of initiators.

4.2. On the link between elaboration process and degradation kinetics

Based on the above, possible explanations of the slower degradation kinetics of EB compared to pp-ANI are:

① the high oxidizability of allylic groups and methine ones in α position of nitrogens because of a very low bond dissociation energy of the C–H involved in radical oxidation.
② the possible residual presence of living free radicals that can possibly initiate the oxidation process.
③ last, the possible existence of nitroxide groups that likely inhibit the oxidation process of emeraldine base as previously mentioned (§4.1.). The latter may also be present in pp-ANI but in lower quantity since the plasma synthesis modifies the nature of repetitive unit.

This explains why pp-ANI oxidizes faster than chemical polyaniline where such unstable groups are not present.

4.3. On the changes of water contact angle

According to Table 2, oxidation contributes to decrease WCA, consistently with the formation of new polar groups inducing an increase of hydrophilicity. Since pp-ANI is also observed to undergo oxidation, the same decreasing trend for WCA is expected. This is however contradictory with experimental results reported in Fig. 6 where WCA for pp-ANI aged under air are observed to increase.

This points out that another phenomenon occurs during pp-ANI ageing under air, and its effects predominate over oxidation ones. Inspiring from works on the degradation of PVC [27], on that of PET exposed successively to the air or inert atmosphere [28] or on that of thermally-aged epoxy-anhydrides [29], the following kinetic explanation can be proposed. Our reasoning is based on the fact that pp-ANI contains a certain quantity of residual living radicals after synthesis. Those radicals can react following two different pathways:

① Under oxygen, they will fast react with oxygen to give a peroxy radical:

$$P^\circ + O_2 \rightarrow POO^\circ \ (k_{OX})$$

Table 2
WCA under air of emeraldine base aged at 200 °C for 10–100 h under air.

Ageing time (h)	WCA (°)
0	74 ± 1.8
10	72.5 ± 2.4
30	66 ± 1.4
50	55 ± 2.2
80	57.5 ± 1.7
100	45.5 ± 1.9

Later, those peroxy radicals will abstract some C–H to give a hydroperoxide, which will give later stable oxygenated compounds such as carbonyls and hydroxyls (Figs. 1 and 2, Scheme 1).

② By coupling, which is an anaerobic process:

$$P^\circ + P^\circ \rightarrow \text{crosslinking } (k_C)$$

In the frame of classical kinetics of radical oxidation processes [30], the rate of each process can be expressed as:

$$r_{OX} = k_{OX}[P^\circ][O_2]$$

$$r_C = k_C[P^\circ]^2$$

so that the competition between both processes can be estimated from the ratio between the reaction rates:

$$r_C/r_{OX} = k_C/k_{OX} \times [P^\circ]/[O_2]$$

It seems reasonable to assume that $[P^\circ]$ increases with the power of the plasma source. It explains why, for ageing at room temperature under air, the increase in contact angle is greater for pp-ANI synthesized at 50 W compared to 10 W (Fig. 6). Reversely, the effects of oxidation are more pronounced for pp-ANI synthesized using 10 W compared to 50 W (Fig. 6) consistently with FTIR results (Fig. 2).

In other words:

- chemical polyaniline mainly oxidizes. Reactions with oxygen induce an increase in hydrophilicity and then decrease WCA.
- polyaniline synthesized by plasma process also undergoes oxidation and subsequent WCA decrease but this is counterbalanced by the crosslinking effect, this latter leading first to an increase in WCA which is favored by the use of a high discharge power increasing the initial quantity of radicals. Then WCA decreases when layers age in air due to oxidation, whereas it remains constant if pp-ANI ages under vacuum where no oxidation can occur.
- it seems that increasing power of plasma synthesis enhances thermal stability, but further investigations are needed.

5. Conclusion

This paper reports a comparison of thermal ageing of a chemical polyaniline (emeraldine base) and a polyaniline synthesized by the plasma technique. The first one was studied at temperatures ranging from 120 to 200 °C under air whereas the second one was studied at room temperature and monitored mainly by FTIR. Both degradations are shown to generate the formation of carbonyl groups. However, the comparison of the formation rate of those latter suggests that pp-ANI degrades much faster than its chemical analog, which is attributed to the existence of structural defects induced by the plasma polymerization process. Degradation was also monitored by the changes in water contact angle, expressing the surface properties. Within the experimental uncertainties, it is observed that conventional polyaniline displays a decrease of WCA, consistently with the appearance of carbonyls and alcohols whereas WCA of pp-ANI displays first an increase ascribed to the crosslinking of plasma-induced radicals and later a decrease induced by the oxidation process. According to the proposed mechanisms, the thermal oxidative ageing induces the disappearance of polarons responsible for the electrical properties of pp-ANI, which might be in principle lost. However, electrical and gas sensitive properties of pp-ANI are usually significantly improved by the use of dopants, the effect of which remains to be investigated. In terms of lifetime prediction methodology, this paper then suggests that the degradation rate of plasma polymers must first be based on a multiscale study of an "ideal" polymer that must be supplemented, in a second step, with the specificities associated to the experimental conditions (discharge power, time on, time off) of the plasma synthesis.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

Declaration of competing interest

We hereby confirm that we have no conflict of interest with the submission of the paper « Thermal oxidative stability of polyanilines ».

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